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Chemical and surface properties of longan seed activated charcoal

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In order to study the chemical compositions and surface properties of longan seed (Daw) activated charcoal, the influences of a phosphoric acid activation process was investigated before and after carbonization. Carbonization temperatures in this study were ranged from 400 - 800°C. It was found that higher carbonization temperatures resulted in a high amount of organic carbon and ashes, while the volatile matters were reversely lowered at higher carbonization temperatures. For carbonization temperatures studied between 400 - 800°C, the activated charcoal possessed a higher iodine number in comparison to the longan seed activated charcoal. Also, the longan seed activated charcoal, being activated by phosphoric acid prior to carbonization, had a greater iodine number than the one being activated by phosphoric acid and then undergoing carbonization. The highest iodine number was obtained from longan seed activated charcoal carbonized at 500°C. Surface properties of activated charcoal showed a loss of its side chains and inherent functionalities while being run through high carbonization temperatures, however, the P-O-C remained intact, especially under carbonization temperatures lower than 700°C. The surface images of the activated charcoal showed more rough.

Key words: Longan seed, carbonization, charcoal, activated charcoal, phosphoric acid.

INTRODUCTION

Activated charcoals are made from materials rich in carbon through carbonization and an activation process. A porous structure and it's adsorption properties can be obtained in carbonaceous materials via either a chemical or a physical process (Gan et al., 2004). Physical activation involves pyrolysis of the source material to produce a charcoal. This is then followed by steam gasification, carbon dioxide or oxygen. Chemical activation involves impregnation with chemicals such as zinc chloride, phosphoric acid, potassium hydroxide, etc., followed by carbonization using the pyrolysis process (Williams and Reed, 2004). Zinc chloride and phosphoric acid are the most commonly used chemical activating agents that are commercially employed. The activating chemical agents act by dehydration of the sample and simultaneously inhibit the formation of tar and volatiles, thereby increasing the charcoal yield during the pyrolysis stage (Williams and Reed, 2004). When using phosphoric acid as the activating agent, some activation is due to the dehydrating power of the acid. During the carbonization stage, the carbon is eroded by being partly oxidised by phosphoric acid, which is reduced to phosphorous and hydrides (Allen et al., 1998).

Longan is classified in the Sapindaceae family by many scientific names: longana lam.; Euphoria longan Strend.; Nephelium longana Camp.; A longan Lour. The mature longan fruit is small (1.5 – 2.0 cm diameter), conical, heart or spherical in shape and light brown in colour. The longan fruit can be eaten fresh, frozen, dried or canned (Mortin, 1987).The waste products of these process are longan seeds and peels.

The aim of the present work was to study the effects of carbonized temperatures, activated temperatures, and pre- or post-impregnation of longan seed charcoal with H_3PO_4 to produce an activated charcoal. The characteristics of the derived activated charcoal, including appro-

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Table 1. Approximate analysis of fresh longan seed and longan seed-charcoal.

Approximate analysis (% dried wt.)	Fresh longan	Longan seed-charcoal Carbonized temperature (°C)				
	Seed	400	500	600	700	800
Ash	1.6	5.9	5.8	6.6	8.8	9.5
Volatile mater (VM)	92.3	9.1	6.3	5.8	2.5	3.0
Organic carbon	7.4	85.0	88.0	87.7	88.7	87.5

ximate analysis, iodine number, surface chemistry by FTIR, and surface morphology by SEM were investigated.

MATERIALS AND METHODS

Material

Longan seed (Daw), as the precursor material, was obtained from the Li district, Lamphun, Thailand. It was well washed with H_2O several times and oven dried at 110°C for 3 h. The dried sample was analyzed for moisture content (ASTM D 2867-95, 1996), ash (ASTM D 2866-94, 1996), volatile matter(ASTM D 5832-95, 1996), and organic carbon (Walkley and Black, 1934). The dried sample was then further analysed using FTIR and a scanning electron microscope to determine functional groups and surface morphology.

Preparation of activated charcoals

The dried longan seed samples were used for the activated charcoal preparation. The activated charcoals were prepared using two methods (modified from Guo and Chong Lua, 1998).

The first method dealt with pre-carbonization and was then followed by phosphoric acid activation. In the pre-carbonization process the dried longan seeds (50 g) were heated to 400, 500, 600, 700 and 800°C for about 1 h under a closed system in a porcelain crucible and then cooled to room temperature. The pre-carbonized charcoal was then subjected to phosphoric acid activation. In the phosphoric acid activation process, the precarbonized charcoal was agitated in 85 wt.% H_3PO_4 (UNIVAR, AR) at a ratio of 1: 0.5 (charcoal : H_3PO_4) prepared weight by volume. After the agitation was finished, the pre-carbonized charcoal slurry was left overnight at room temperature and, then, dried at 110°C for 24 h. The samples were then activated in a closed system. Next, the samples were heated to five temperatures ranging from 400, 500, 600, 700 and 800°C to optimize the heat treatment. It was maintained at a constant temperature for 1 h before cooling. After cooling down, the activated charcoal was washed several times with 0.2 N HCl, then with hot water until the pH became neutral, and finally with cold water to remove the excess phosphorous compounds. The washed samples were dried at 110°C to get the final product. This product was labeled as PCLGAC.

The second method began with the dried longan seed (50 g) pre-impregnated in 85 wt.% H_3PO_4 at a ratio of 1:0.5 prepared weight by volume basis. The process continued similarly to the first method. The final product from the second method was labeled as PILGAC.

The charcoal and activated charcoal were analyzed for iodine number, FTIR spectra, and surface morphology.

Measurement of iodine number

The iodine number was measured following the method of Abe et al. (2001). Charcoal and activated charcoal were ground into a powder and filtered through a 45 μm sieve. The filtered powders were washed with distilled water, then dried at 110°C for 24 h, and eventually kept in a desiccator containing silica gel. A certain amount of charcoal or activated charcoal was added to 50 ml of a 0.05 M iodine solution and the mixture was shaken regularly for 15 min at room temperature. After centrifugation, 10 ml of supernatant was titrated with 0.1 M of sodium thiosulfate to determine the equilibrium concentration of iodine C (g/l) and the amount of iodine adsorbed onto carbon X (mg/g). An adsorption isotherm of iodine onto the microporous charcoal was approximated by the Freundlich equation: $\log X = \log K + (1/N) \log C$, where K and 1/N are adsorption constants. Iodine adsorption capacity was determined using the adsorption isotherm as the amount of iodine adsorbed onto microporous carbon at C = 2.5 g/l.

FTIR studies

The FTIR spectra were recorded on a Spectrum GX, Perkin Elmer, U.S.A. Fourier transform Mid/far IR system. Samples were mixed with finely divided spectrograde patassium bromide (Fisher Scientific) at the ratio of 1:50 to enable absorbance values of less than one to be recorded. Spectra were recorded at a resolution of 4 cm^{-1} using a minimum of 400 scans. Background spectra of potassium bromide and water vapour were recorded every 100 min.

Surface morphology

Scanning electron microscopy was used to visualise the surface morphology of the charcoal samples. The samples were scanned by a LEO 1455 VP electron microscopy, England, scanning electron microscope. The samples were coated with gold by a gold sputtering device for a clear vision of the surface morphology.

RESULTS AND DISCUSSION

Chemical analysis

A chemical analysis comparison was made between fresh longan seed and charcoals made from longan seed at different carbonization temperatures, see Table 1, ash contents of charcoals continued to increase with increased carbonization temperatures. For example, when the carbonization temperatures moved from 400 to 800°C there was an increase in ash content from 5.9 to 9.5% by dried weight. This was believed due to lowered volatile matter (VM). Charcoal carbonized at a temperature of 400°C had VM at about 9.1% and the VMs lowered to 3.0% when the carbonization temperature was increased to 800°C. These findings coincided with the

Table 2. Percentage yield and iodine number of charcoal and activated charcoal from longan seed.

Carbonized temperature °C	% yield of Charcoal	Iodine number (mg I_2/g charcoal or activated charcoal)		
		charcoal	PCLGAC	PILGAC
400	38.9	412.8	452.3	547.3
500	32.9	384.9	432.9	556.7
600	27.4	374.2	405.1	537.1
700	25.1	430.9	401.6	515.0
800	22.2	426.2	360.2	512.0
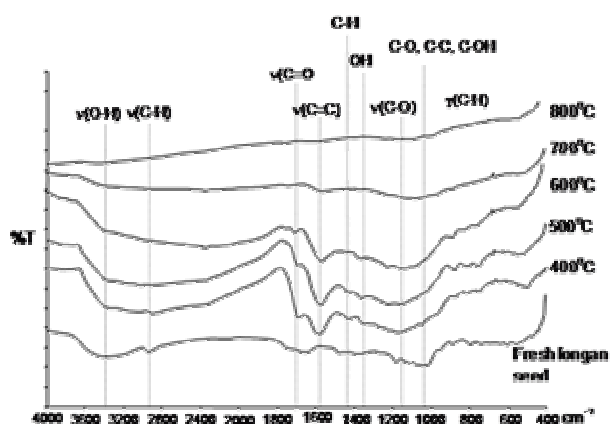
Figure 1. FTIR spectra of fresh longan seed and longan seed charcoals with carbonized temperatures at 400 - 800°C.

previous studies on pistachio-nut shell (Lua and Yang, 2004) and banana peel (Mopoung, 2005) which indicated that the lowering of the amount of VM will create a high percentage of calculated ash because the ash is non-volatile. When carbonization temperatures were raised from 400 to 600°C, it led to a considerable reduction of VM, whereas with continuously raising temperatures from 600 to 800°C, the degree of reduction of VM was almost negligible. Presumably, this resulted from a "burn-off" phenomena (Gan et al., 2004).

Table 2 show tha, the amount of carbonaceous substance under carbonization temperatures between 400 to 800°C was lowered from 38.9 to 22.2% because of the high amount of VM being driven off. These finding also coincide with the previous observations of pistachio-nut shells (Lua and Yang, 2004) and rubber wood sawdust (Srinivasakannan and Abu Bakar, 2004) which increased the incomplete carbonization process believed to occur at low carbonization temperatures.

In Table 2, it was seen that the iodine number of carbonized longan seed at temperatures ranging from 400 to 800°C were lower than increased carbonization tempera-

temperatures e.g. at 400, 500, and 600°C which possessed iodine numbers of 412.8, 384.9 and 374.2 mg/g, respectively. The assumption was that because of the incomplete carbonization process at 400°C, the tar left over contributed to iodine absorption (Arenas and Chejne, 2004). The iodine number was found to be highest at 430.9 mg/g under a carbonization temperature of 700°C. Nonetheless, at a carbonization temperature of 800°C, the iodine number was lowered because of the damage to the wall structure of the activated charcoal (Lua and Yang, 2004). Ash contents were greater at higher carbonization temperatures, because ash can be absorbed by a porous structure, and restrict iodine molecules (Pastor-Villegas et al., 1999). Iodine numbers of PCLGAC and PILGAC were greater when compared to the longan seed charcoal being carbonized under every studied temperature, except carbonized temperatures of 700 and 800°C. It was seen that a carbonization temperature higher than 600 C lowered the iodine number due principally to either the collapse of the carbonaceous structure or the bending of the porous structure. The squeezed porous structure at higher carbonization temperatures strengthened (Guo and Chong Lua, 1998). Furthermore, it was clear that the iodine number of PILGAC was greater than that of PCLGAC due to the phosphoric acid destroying the aliphatic and aromatic species present in fresh longan seed, and therefore swiftly removing the volatile matters during the carbonization process (El-Hendawy, 2006). Thus it is believed that the activated charcoal made from longan seed should be first activated using phosphoric acid without any prior carbonization in order to reduce costs. The proper carbonization temperature for longan seed is recommended at 500°C, and this is similar to the best carbonization temperature for chesnut wood (Gómez-Serrano et al., 2005).

FT-IR spectra

In Figure 1, FTIR spectrums of fresh longan seed represent the spectrum bands of ν(O-H) at 3370.49, ν(C-H) at 2927.67 cm^{-1}, ν(C=O) at 1722.67 cm^{-1}, ν(C=C) at 1635.01 cm^{-1}, ν(C-O) or C-C or C=O at 1230.27-921.82 cm^{-1}, δ(C-H) at 1456.66, and γ(C-H) at 708.92-527.70 cm^{-1} (Lua and Yang, 2004). The band 3370.49 cm^{-1} is attributed to the hydroxyl groups in phenolic and aliphatic structures. The band 2927.67 cm^{-1} is CH stretching in aromatic methoxyl groups and in methyl and methylene groups of side chains. The band of the carbonyl group inketones, aldehydes or carboxyl appears at 1722.67 cm^{-1}. The band at 1635.01 cm^{-1} may originate from carbohydrates. The bands at 1230.27-921.82 cm^{-1} is associated with C-O, C-C stretching and C-OH bending in polysaccharides (Fierro et al., 2007). The in depth study
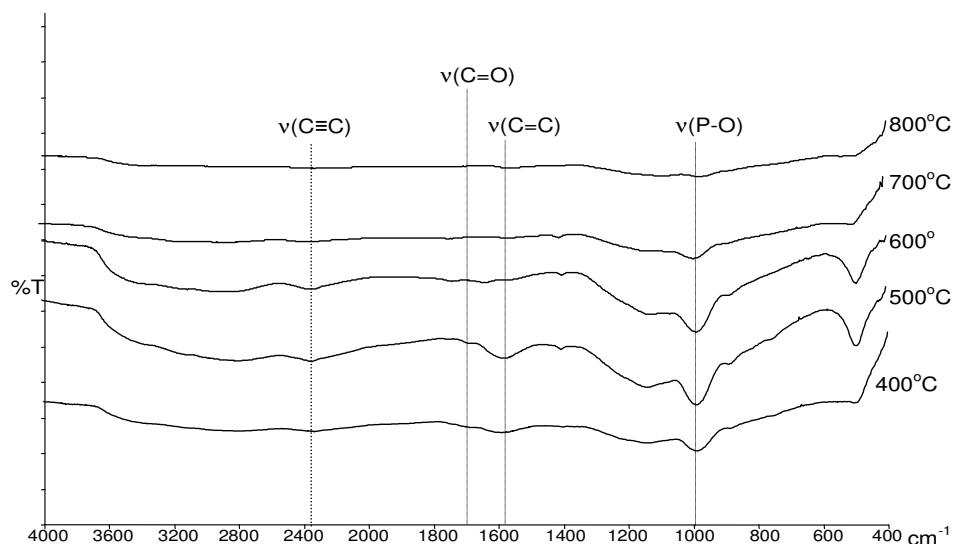
Figure 2. FTIR spectra of PCLGACs with activation at carbonized temperatures of 400 to 800 °C.
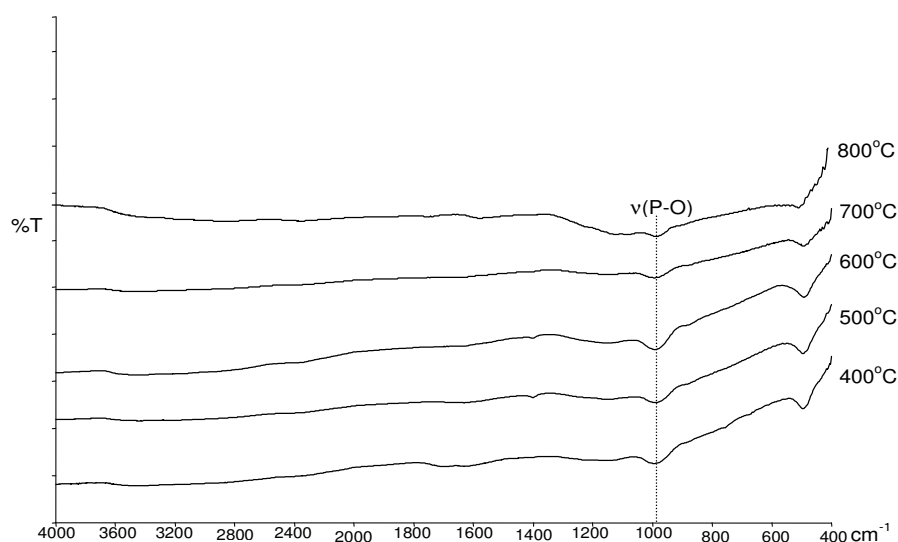

Figure 3. FTIR spectra of PILGACs with activation at carbonized temperatures of 400 to 800 °C.

of the longan charcoal carbonized between 400 to 800 °C, especially narrowing to 700 - 800 °C, had a very weak band of FTIR spectrums (Figure 1), so that the side chains were removed by the lowering of volatile components as showed in Table 1. This finding also supported the wood tar pitches (Prauchner et al., 2005).

Weak bands of the FTIR spectrum at 2918.05 cm^{-1} of ν (C-H), 1697.88 cm^{-1} of ν(C=O), and at 1178.18 plus 1054.54 cm^{-1} of ν(C-O) represented the existence of the above functionalities at carbonization temperature of 400 °C. The spectrum band was visible at 1589.73 and 1433.90 cm^{-1} which was the possession of ν (C=C), therefore, the absence of some functionalities such as – H, =O, -O and reproducing C=C. At carbonization temperature of 700 °C, there were weak but visible bands of C≡C at 2345.77 cm^{-1} and C=C at 1557.87 cm^{-1}. However there were very weak spectrum bands at 1739.02 and 1074.84 cm^{-1} which possessed ν(C=O) and ν(C-O), respectively. This was believed to be the result of the combustion of carbon and oxygen during the carbonization process. Moreover, the FTIR spectra of activated charcoal which was triggered by phosphoric acid after the
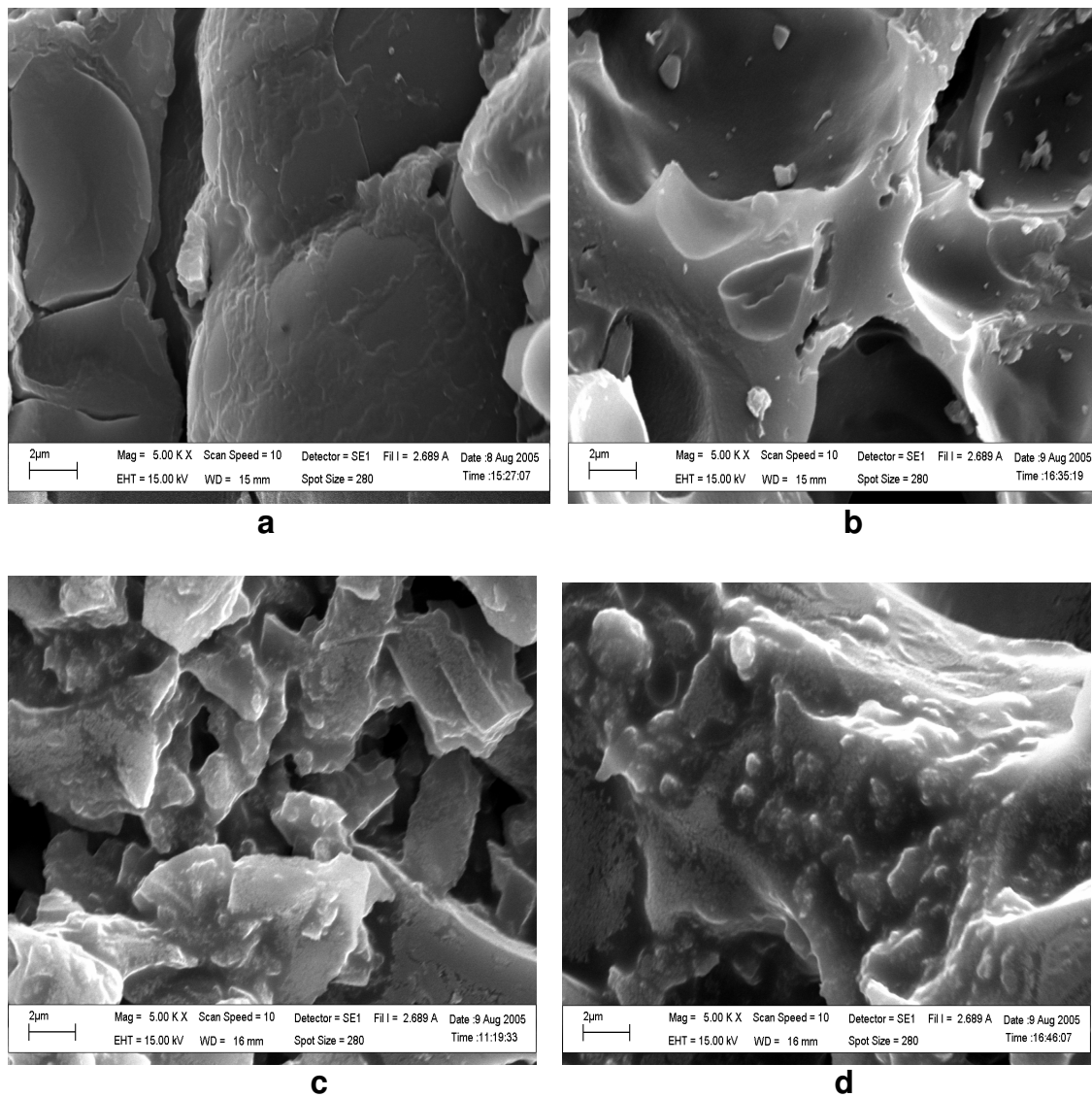
Figure 4. Scanning electron micrographs at a magnification of x5000 of (a) fresh longan seed (b) longan seed charcoal with carbonized temperature at 500°C (c) PILGAC carbonized temperature at 500°C (d) PCLGAC with activation at carbonized temperature of 500°C.

carbonization process, (Figure 2), and the phosphoric activation of fresh longan seed (Figure 3), demonstrated very weak spectrum bands at 2349.16-2334.02 cm^{-1} (C≡C), 1590.17-1571.09 cm^{-1} (C=C). However, activated charcoal represented a clear spectrum band of 993.27-975.05 cm^{-1} (ionic phosphate group) for carbonization temperatures between 400 to 600°C and an unclear band for carbonization temperatures between 700 to 800°C. It was thought that the results came from the presence of the strong bonding of phosphate and carbon atoms (P-O-C) that the cleansing by acid cannot remove (McKee et al., 1984; Guo and Rockstraw, 2007; Budinova et al., 2006). Nevertheless, the bonding can be lessened when the carbonization temperatures is higher than 800°C (Haimour and Emeish, 2006).

Scanning electron micrography

Referring to Figure 4a, it was seen that the bulk body of fresh longan seed was highly packed, porous-less, and having no cavities. After having been carbonized under 500°C, see Figure 4b, a poriferous structure was apparent due to volatile matters being driven off. However, material substances and tars were found attached to the walls and some residues were possibly condensed during incomplete carbonization (El-Hendawy, 2006). The poriferous diameter ranged from 15 - 40 μm. When activated charcoal was infused by phosphoric acid and underwent further carbonization, under 500°C, (Figure 4d), the residues clinging to the walls of PCLGAC disappeared and had rouged (Figure 4c). Fine and a squarer shape of

PILGAC can be formed by phosphoric acid activation, thereby creating more surface and a higher iodine number, particularly at a carbonization temperature of 500°C.

Conclusion

Longan seed was carbonized to form longan seed activeted charcoal. A carbonization temperature of 500°C was favorable due to the highest presence of organic carbon. Longan seed activated charcoal which was carbonized at 500°C and was first triggered using phosphoric acid at the ratio of 1.0:0.5 by weight of charcoal per volume of phosphoric acid which yielded a activated charcoal with a higher iodine number, compared to non-activated charcoal that were carbonized between 400 - 800°C. Activated charcoal which was triggered by phosphoric acid prior to the carbonization process will give a higher iodine number than that being triggered after the carbonization process, particularly at carbonization temperature of 500°C. Therefore, it is recommended to activate longan seed using phosphoric acid, thereafter carbonization is made at 500°C which can enormously reduce energy consumption. Upon increasing carbonization temperatures, the side chain groups and inherent functionalities vanished, however, P-O-C remained intact if the carbonization process was employed at a temperature lower than 700°C. The surface images of activated charcoals have rough.

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